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<b>(21) International Application Number:</b> PCT/GB98/01210 <b>(22) International Filing Date:</b> 24 April 1998 (24.04.98) <b>(30) Priority Data:</b> 9709268.8                      8 May 1997 (08.05.97)                      GB <b>(71) Applicant (for all designated States except US):</b> IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chem- ical House, Millbank, London SW1P 3JF (GB). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> EWING, Paul, Nicholas [GB/GB]; 14 Alexandra Road, Stockton Heath, Warrington WA4 2UT (GB). MCCARTHY, John, Charles [GB/GB]; 63 Grange Drive, Penketh, Warrington, Cheshire WA5 2JN (GB). <b>(74) Agents:</b> GEARY, Stephen et al.; ICI Group Intellectual Property, The Heath, P.O. Box 11, Runcorn, Cheshire WA7 4QE (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> A PROCESS FOR THE PRODUCTION OF A HYDROFLUOROCARBON AND USE OF A CATALYST THEREFOR <b>(57) Abstract</b>  A process for the production of R227ea by the liquid-phase catalytic fluorination of hexafluoropropene in which the catalyst comprises a Lewis acid transition metal fluoride, for example tantalum pentafluoride and niobium pentafluoride, is disclosed. The catalyst provides an alternative to antimony pentafluoride as a liquid phase fluorination catalyst thus avoiding the formation of HSBF <sub>6</sub> and provides excellent selectivity. A catalyst precursor comprising a Lewis acid transition metal halide is also disclosed.		

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A Process for the Production of a Hydrofluorocarbon and Use of a Catalyst Therefor

This invention relates to a process for the production of a hydrofluorocarbon and a catalyst for its production. In particular, the invention relates to a process for the production of a hydrofluorocarbon for example heptafluoropropane by the catalytic fluorination of a hydrofluoroalkene, for example hexafluoropropene and to a catalyst containing a transition metal compound for use in this process.

Hydrofluorocarbons, for example 1,1,1,2,3,3,3-heptafluoropropane, (which is known as Refrigerant 227ea and will be referred to herein as R227ea for convenience), have found utility in many fields as replacements for chlorofluorocarbon compounds on account of the zero ozone depletion potential. Such applications include use in medical applications for example, as an aerosol propellant, use as a fire suppressant, use in refrigeration applications and in other applications. R227ea is especially useful in such applications as it has a zero ozone depletion potential. R227ea is particularly beneficial in medical applications in view of its combination of properties of low toxicity, non-flammability, solvent properties and boiling point. For medical applications it is required that the hydrofluorocarbon be of very high purity.

It is known to produce hydrofluorocarbons by the hydrofluorination of a fluoroalkene to the corresponding fluoroalkane, optionally in the presence of a catalyst, in the liquid phase or vapour phase. Hydrogen fluoride is known for use as a hydrofluorination agent in such processes.

A range of materials may be employed as catalysts in hydrofluorination processes. For example chromia may be employed in vapour phase processes and carbon is also known for such use but has the drawback that it requires a high reaction temperature and may rapidly deactivate.

Catalysts containing antimony pentafluoride optionally together with hydrogen fluoride are known for use as a fluorinating agents in liquid phase processes but have the disadvantage that a highly corrosive substance,  $\text{HSbF}_6$ , may be formed.  $\text{HSbF}_6$  is one of the most corrosive materials known to man.

WO 96/02483 discloses a process for the production of R227ea by the reaction of hexafluoropropene with anhydrous hydrogen fluoride in the presence of an antimony catalyst, in particular the catalyst preferably contains antimony pentafluoride as evidenced by all of the examples in this document. However, the presence of hydrogen fluoride

together with antimony pentafluoride is known to generate  $\text{HSbF}_6$ . As such, the process suffers from the drawbacks inherent in handling a highly corrosive substance such as chemical attack on the internal surfaces of the production plant. This may be mitigated by employing specialised materials of construction but these are often prohibitively  
5 expensive.

There remains a need for a catalyst which provides effective liquid phase fluorination, which does not cause the formation of  $\text{HSbF}_6$  and which enables R227ea to be produced to a high level of purity. We have now determined that transition metal fluorides which act as Lewis acids provide excellent fluorination catalysts in the  
10 production of R227ea and do not lead to the formation of  $\text{HSbF}_6$ .

Accordingly, a first aspect of the present invention provides a use of a catalyst which comprises a Lewis acid transition metal fluoride in a process for the production of R227ea by fluorination of hexafluoropropene.

A second aspect of the invention provides a process for the production of R227ea by  
15 the catalytic fluorination of hexafluoropropene which comprises contacting hexafluoropropene with a catalyst in the presence of a fluorinating agent in the liquid phase in which the catalyst comprises a Lewis acid transition metal fluoride whereby R227ea is produced.

By "Lewis acid transition metal fluoride" we mean a compound containing a  
20 transition metal and at least one fluorine atom and which may also contain other halogens, for example chlorine, and which exhibits Lewis acid properties as defined in Chem. Rev., 78, pp1 - 22 (1978) by Jensen.

The catalyst comprises a Lewis acid transition metal fluoride. The transition metal is suitably selected from any one of Groups IIIa to VIIa, preferably Group Va, of the Periodic  
25 Table and preferably from Periods 5 and 6. In a preferred embodiment of the invention the transition metal preferably comprises tantalum, niobium or mixtures of tantalum and niobium. Optionally other metals or compounds thereof may also be included in the catalyst together with the transition metal.

The ligands of the catalyst comprise at least one fluorine atom. The other ligands are  
30 not critical provided that the catalyst exhibits Lewis acidity and is stable in the reaction medium. It is nevertheless preferred that the other ligands are all halogen and especially preferred that they all be fluorine.

In a preferred embodiment, the catalysts in the present invention comprise tantalum pentafluoride and niobium pentafluoride.

\* The catalyst may be employed "as is" or a catalyst precursor may be employed in the process and converted to the desired fluoride catalyst before and/or during the reaction in order to produce a Lewis acid transition metal fluoride as the catalytic species. Such treatment may be effected using any suitable fluorine-containing material provided that this does not cause deactivation of the catalyst. Hydrogen fluoride is especially preferred for such treatment.

The invention provides, in a third aspect, the use of a Lewis acid transition metal halide as a catalyst precursor for conversion to a Lewis acid transition metal fluoride catalyst before and/or during a process for the production of R227ea by the catalytic fluorination of hexafluoropropene.

A further aspect of the invention provides a process for the production of a catalyst comprising a Lewis acid transition metal fluoride for use in the production of R227ea by the catalytic fluorination of hexafluoropropene which process comprises contacting a Lewis acid transition metal halide with a fluorine-containing material whereby at least one halogen ligand in the Lewis acid transition metal halide is replaced by a fluorine ligand.

In the process according to the second aspect of the invention, the fluorinating agent suitably comprises hydrogen fluoride. Preferably the fluorinating agent is anhydrous in order to reduce or avoid deactivation of the catalyst.

Suitably R227ea is produced in the process according to the second aspect of the invention at a selectivity of at least 99.5% and often in excess of 99.8%. This compares well with known vapour phase processes, for example as disclosed in WO 96/02483 in which a selectivity of the order of 99.3% is exemplified.

The liquid phase fluorination of hexafluoropropene according to the present invention is suitably carried out at a temperature in the range 20 to 200°C, preferably 40 to 120°C and especially 50 to 100°C. Suitably the reaction is carried out at superatmospheric pressure, and at such a pressure that the reactants are in the liquid phase for sufficient time to react to produce R227ea. Preferably the pressure is at least 5 bar and more preferably the pressure is 10 to 50 bar.

The residence time is sufficient to permit conversion of hexafluoropropene feedstock to R227ea. The required residence time will be dependent on the degree of conversion

required and also influenced by the ratio of reactants and reaction conditions. If a low conversion is employed, for example to operate at milder reaction conditions it is preferable that the feedstocks be recycled to increase the yield of R227ea from the starting material. Recycle may also be employed if high single pass conversions are required.

- 5 Selectivity to R227ea may be enhanced further by employing a lower conversion rate as milder reaction conditions typically suppress the formation of by-products.

Suitably the molar ratio of HF to hexafluoropropene (HFP) fed to the reactor is at least 1:1 and preferably 1.2 to 10:1. If a lower conversion rate is required a molar ratio of HF to HFP of 0.1 up to 1:1 may be employed.

- 10 Suitably the molar ratio of HFP to the catalyst is not more than 100:1 and is preferably 1 to 50:1.

The levels of HF, HFP and catalyst are suitably selected such that the catalyst and reactants remain dissolved in the liquid phase under the reaction conditions employed.

- The R227ea product is suitably removed from the process in the vapour phase and  
15 may be subjected to conventional separation and/or purification processes as desired downstream from the reaction stage. Unreacted starting materials or by-products obtained from any such downstream treatment or purification may be recycled to a point upstream of the reactor stage to improve product yield and to decrease the production of effluent from the process.

- 20 The process according to the second aspect of the invention may be operated in batch or continuous mode as desired. Semi-batch operation may also be employed in which one or more feedstocks are fed continuously to the process and one or more other feedstocks are fed to the process in batch-wise fashion.

The invention is illustrated by the following non-limiting examples.

25 Example 1

A 150ml Monel reaction vessel was charged with 60.2g of Hexafluoropropane (HFP), 10.4g of anhydrous hydrogen fluoride and 11.1g of TaF<sub>5</sub> and heated at 72C for 4.5 hours under autogenous pressure. A sample was removed from the reactor and treated to remove hydrogen fluoride. Analysis of the sample gave the following results:

- 30 HFP conversion = 81.4%  
Selectivity to HFC 227ea = 99.88%

Example 2

The procedure of Example 1 was repeated with a charge of 61g of HFP, 9.9g of HF and 10.8g of TaF<sub>5</sub>, at a reaction temperature of 45 - 50C. After 4.75 hours, a 15.8% conversion of HFP to HFC 227ea was achieved.

- 5        The results presented illustrate that HFC 227ea is produced by the process of the present invention. The results also illustrate that the rate of production of HFC 227ea is significantly increased by conducting the process at a temperature in excess of 50C.

Claims

- 1 Use of a catalyst which comprises a Lewis acid transition metal fluoride in a process for the production of R227ea by fluorination of hexafluoropropene.
- 2 Use according to claim 1 in which the transition metal is selected from any one of  
5 Groups IIIa to VIIa of the Periodic Table.
- 3 Use according to claim 2 in which the transition metal comprises tantalum, niobium or mixtures of tantalum and niobium.
- 4 Use according to any preceding claim in which the catalyst comprises at least one fluorine atom.
- 10 5 Use according to any preceding claim in which the catalyst is selected from tantalum pentafluoride and niobium pentafluoride.
- 6 Use of a Lewis acid transition metal halide as a catalyst precursor for conversion to a Lewis acid transition metal fluoride catalyst before and/or during a process for the production of R227ea by the catalytic fluorination of hexafluoropropene.
- 15 7 A process for the production of a catalyst comprising a Lewis acid transition metal fluoride for use in the production of R227ea by the catalytic fluorination of hexafluoropropene which process comprises contacting a Lewis acid transition metal halide with a fluorine-containing material whereby at least one halogen ligand in the Lewis acid transition metal halide is replaced by a fluorine ligand.
- 20 8 A process for the production of R227ea by the catalytic fluorination of hexafluoropropene which comprises contacting hexafluoropropene with a catalyst in the presence of a fluorinating agent in the liquid phase in which the catalyst comprises a Lewis acid transition metal fluoride whereby R227ea is produced.
- 9 A process according to claim 9 in which the fluorinating agent comprises hydrogen  
25 fluoride.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01210

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C17/087 C07C19/08 B01J27/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 258 225 A (FEIRING ANDREW E) 24 March 1981 see claims; example 23	1-9
X	WO 89 12615 A (DU PONT) 28 December 1989 see page 7, line 17 - line 24; claim 1	1,6,7

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
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Authorized officer

Bonnevalle, E

# INTERNATIONAL SEARCH REPORT

Information on patent family members

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